

## AMORPHOUS MATERIALS†

# An experimental study of phosphorous and aluminosilicate speciation in and partitioning between aqueous fluids and silicate melts determined in-situ at high temperature and pressure

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## ABSTRACT

The structure of phosphorus-bearing, H<sub>2</sub>O-saturated silicate melts, silicate-saturated aqueous fluids, and silicate-rich single phase (supercritical) liquids has been characterized in situ to 800 °C and 1486 MPa in an Ir-gasketed hydrothermal diamond-anvil cell (HDAC) with the aid of both confocal microRaman and FTIR spectroscopy. Temperature and pressure in the HDAC were recorded with thermocouples ( $\pm 1$  °C uncertainty) and pressure- and temperature-dependent Raman shift of <sup>13</sup>C diamonds ( $\pm 40$  MPa uncertainty). Starting materials were aluminum-free Na<sub>2</sub>O·4SiO<sub>2</sub> (NS4) and with 10 mol% Al<sub>2</sub>O<sub>3</sub> (NA10) substituting for SiO<sub>2</sub>, both with 5 mol% P<sub>2</sub>O<sub>5</sub>.

Aluminosilicate species of Q<sup>0</sup>, Q<sup>1</sup>, Q<sup>2</sup>, and Q<sup>3</sup> type exist in coexisting fluid and melt and in single phase liquid together with phosphate species, PO<sub>4</sub>, P<sub>2</sub>O<sub>7</sub>, and Q<sup>n</sup>P. In the Q<sup>n</sup>P species, n O atoms bridge between Si<sup>4+</sup> and P<sup>5+</sup>, whereas there is no Si-to-P linkage in the PO<sub>4</sub> and P<sub>2</sub>O<sub>7</sub> species. In melts, the abundance of the most depolymerized silicate species, Q<sup>0</sup>, is positively correlated with temperature and pressure, whereas that of the most polymerized species, Q<sup>3</sup>, decreases with temperature and pressure. In the silicate solute of aqueous fluids, the opposite relationship exists with Q<sup>0</sup> abundance decreasing and Q<sup>3</sup> (and Q<sup>1</sup> and Q<sup>2</sup>) abundance increasing with increasing temperature and pressure. The silicate melts, therefore, become increasingly depolymerized and the silicate solute in aqueous fluids decreasingly depolymerized because increasing H<sub>2</sub>O solubility in melts causes melt depolymerization, whereas increasing silicate solute abundance in fluids results in silicate polymerization. The P<sub>2</sub>O<sub>7</sub> and Q<sup>n</sup>P are the dominant phosphate species in fluid, melt, and single phase liquid with orthophosphate, PO<sub>4</sub>, playing a subordinate role. The fluid/melt partition coefficients for P<sub>2</sub>O<sub>7</sub> and Q<sup>n</sup>P species are in the 0.15–0.7 range with that of Q<sup>n</sup>P being greater than that of P<sub>2</sub>O<sub>7</sub>. The PO<sub>4</sub> fluid/melt partition coefficients are <0.2. In all cases, the partition coefficients increase with increasing temperature and pressure. There is no clear influence of Al<sub>2</sub>O<sub>3</sub> on partition coefficients. Hence, it appears that P-bearing complexes in fluids and melts are associated with Na<sup>+</sup> that becomes available as silicate species polymerize. The mobility of phosphorus during metamorphic processes is principally governed by the availability of alkali metals (and perhaps alkaline earths).

**Keywords:** Phosphate solution, melt structure, aqueous fluid, fluid/melt partitioning